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Influence of the coal-derived synthesis gas composition on the thermal stability of ZnO sorbents in the desulfurization process

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Abstract. The priority direction of thermal energy on solid fuels is to increase efficiency and environmental safety, approaching zero emissions of harmful substances. To achieve these goals, they are currently creating new schemes for combined cycle gas turbine units with intra-cycle gasification (IGCC). To improve the efficiency of the IGCC cycle, hot dry desulfurization (HGC) technologies are being developed. HGC uses regenerable sorbents that allow the repeated adsorption of hydrogen sulfide from synthesis gas, among which the most acceptable thermodynamic and operational characteristics are based on ZnO sorbents. The article uses the method of thermogravimetric analysis (TGA) to investigate the development of target reaction capture hydrogen sulfide ZnO-containing sorbent and sorbent reactions with components of synthesis gas in the temperature range up to 1000°C. The sorbent calcined at 900°C shows thermal stability in an inert atmosphere over the entire temperature range studied. Uncalcined sorbents at temperatures of 200 and 600°C emit carbon dioxide in an amount of 1.5-4.5% by weight of the sorbent. At temperatures up to 550°C, the target reaction is basic, and side reactions practically do not develop. The maximum rate of absorption of hydrogen sulfide by the sorbent is observed at a temperature of 600°C. At 500-550°C reactions of a sorbent begin with H₂ and CO, at 750-800°C – with carbon, at 850°C – with CH₄. The intensity of effect of reagents is defined on degradation of a sorbent by reactionary ability of gases more than temperature.

1. Introduction

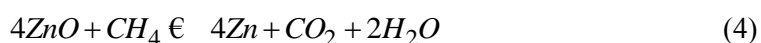
The priority direction of thermal energy on solid fuels is to increase efficiency and environmental safety with the approach to near-zero emissions. To achieve these goals, they are currently creating new schemes for combined cycle gas turbine units with intra-cycle gasification (IGCC), as an alternative to direct fuel combustion. The synthesis gas produced in the IGCC gasifier must be purified from harmful impurities to the minimum concentrations that meet the requirements for the purity of the fuel gas when gas turbines are burned in the combustion chamber [1]. There is a tendency to switch from cold wet gas cleaning to hot dry HGC (hot gas cleanup) at intervals of 300-400°C to 1000°C and higher, since this increases the thermodynamic efficiency of the IGCC cycle by 1.8-2.5% [2,3]. In gas clean up studies in IGCC schemes, hot gas purification methods are of particular interest. The most costly gas cleaning processes include the removal of sulfur compounds contained in synthesis gas mainly in the form of H₂S hydrogen sulfide with concentrations of 0.5 ml/l to 30 ml/l and more, depending on the grade of gasifiable fuel [4]. HGC uses regenerated sorbents that allow



multiple reversible adsorption of sulfur from hydrogen sulfide synthesis gas, among which the sorbents based on ZnO have the most acceptable thermodynamic and operational characteristics, having a high affinity for H₂S and having a working temperature range of 250-650°C, sulfur content at the level 200-300 g/kg and the degree of purification from H₂S to <7 ppm [5-7]. Sulfur from a multicomponent synthesis gas is absorbed by several reactions, the main of which is the target reaction with H₂S:



In addition to the target reaction, non-sulfur-containing components of the synthesis gas (H₂, CO, CH₄) and condensed carbon can enter into complex interactions with the sorbent in the so-called side reactions (2) - (5), accompanied by release of metallic zinc, its evaporation and destruction or rebirth sorbent.



The currently existing calculation methods as a rule do not take into account the effect on the cleaning process of side reactions, as well as the reverse processes [8, 9], and the behavior of sorbents is usually studied on model gases [10, 11], or only the target reaction is considered [12-14]. In the article, the method of thermogravimetric analysis (TGA) traces the development of direct side reactions (2)-(5), compares with the target reaction (1), determines the beginning and rate of the thermochemical degradation of the ZnO-containing sorbent.

2. Materials and method

2.1. Materials

As a sorbent, granulated (granule diameter 3 mm) and crushed (diameter less than 200 microns) ZnO-sorbent Katalco Johnson & Matthey 32-4 and zinc oxide powder (diameter less than 50 microns) were used. According to the data of scanning electron microscopy, in addition to Zn and O, Fe, Al and Ca are present in the range of 3-8% by weight of Katalco sorbent. Zinc oxide powder is 100% zinc and oxygen. The distribution of elements on the sample surface is uneven. The ratio of zinc atoms and oxygen in two measurements is 0.84-1.67 for Katalco and 1.29-1.92 for ZnO powder.

In experiments on TGA, gas mixture reagents hydrogen sulfide-argon (1% vol. H₂S), hydrogen argon (9.5% H₂), carbon monoxide-nitrogen (70% vol. CO), methane-argon (4.8% vol. CH₄), hydrogen. The solid reagent was BAU-A activated charcoal powder.

2.2. Method

The thermostability experiments were carried out on a NETZSCH STA 449F3 instrument with a standard TG holder and a QMS 403C Aëolos quadrupole mass spectrometer. The sample mass of the sorbent was 20-25 mg, the flow rate of the gas mixture - 100-133 ml / min. The sample heating rate was 15 and 20 K/min. The temperature limit of thermal stability (the beginning of a significant decomposition of ZnO) was estimated by the relation:

$$R_\tau = \frac{1}{m_\tau - m_{\text{end}}} \cdot \frac{dm}{d\tau} > 0.0001$$

Where m_τ is the mass of the sample at the current time, m_{end} is the mass of the inert residue.

The experiments were carried out in three stages. At the first stage, the effect of sorbent calcination (30 min, 900°C, air) on thermal stability in a neutral medium (argon) was evaluated. Previously, for calibration of the instrument, the baseline was removed without a sorbent, the resulting curve was subtracted from the subsequent experimental results.

At the second stage, the course of the direct target reaction (1) of the absorption of hydrogen sulfide by zinc oxide was recorded.

At the third stage, the flow of direct side reactions (2) - (5) of the synthesis gas purification process was studied: reduction of zinc oxide in hydrogen, carbon monoxide, methane and carbon separately.

3. Results and discussion

3.1. Behavior of the sorbent in a neutral environment

The calcined sorbent throughout the entire temperature range (250-1000°C) shows thermal stability (curve 1 in figure 1). According to the Ellingham diagram, zinc oxide dissociation occurs at temperatures above 2000 K. There is no gas output from the calcined sorbent. The uncalcined sorbent in the process of heating loses from 1.5 to 4.5% by weight, which is associated with local peak emissions of adsorbed gases and vapors (CO_2 , H_2O). ZnO powder gives low-temperature (250°C) emissions of CO_2 (curve 5) and H_2O . The crushed and granulated sorbent has a more pronounced medium-temperature (600°C) peak (curves 6 and 7). The release of H_2O in non-powder sorbents was not observed.

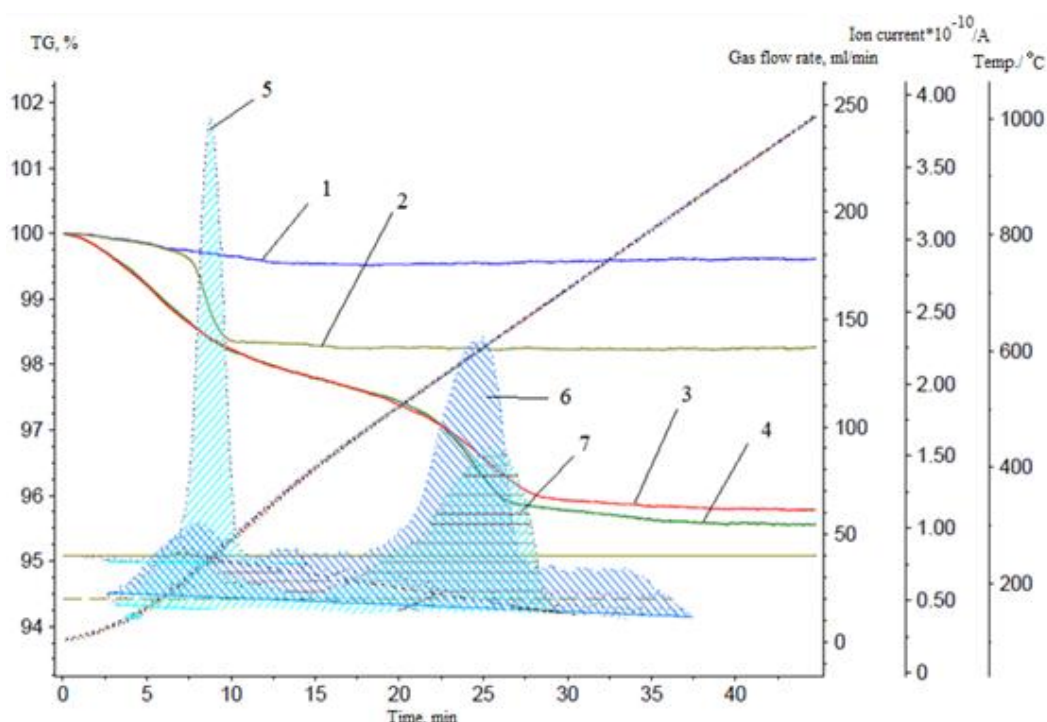


Figure 1. The results of TGA sorbents in argon: 1 - calcined crushed, 2 - uncalcined zinc oxide powder, 3 - uncalcined crushed sorbent, 4 - uncalcined granulated sorbent, 5 - carbon dioxide emission from the uncalcined powder, 6 - carbon dioxide emission from the uncalcined crushed sorbent, 7 - emission of carbon dioxide from uncalcined granulated sorbent.

3.2. Behavior of the sorbent in active media

At a temperature of 350°C, the target reaction (1) begins. At 800°C, the target reaction is completed by saturation of the sorbent with an increase in mass of 16%. The maximum absorption rate at a temperature of 600°C.

In the temperature range of 500–1000°C, side reactions (2)-(5) develop, accompanied by significant mass loss. The sorbent exhibits the smallest temperature stability with respect to the main component of synthesis gas - hydrogen. A noticeable destruction of the sorbent in a mixture of hydrogen and argon begins at a temperature of 500-550°C. (figure 2). At close temperatures, the reaction of ZnO with carbon monoxide is activated (figure 2).

Carbon begins decomposition of ZnO at temperatures above 800°C (figure 2). The process is accompanied by the active release of CO₂ and the absorption of an oxygen impurity. At the end of the experiment, excess carbon remains in the crucible.

Methane, which is present in raw IGCC synthesis gases in insignificant quantities, acts on the sorbent in two ways. That part of methane, which is on the way from the gas generator to the gas clean up is subjected to thermal decomposition, is entered into the desulfurization reactor in the form of black carbon and hydrogen and acts according to reactions (5) and (2).

The other part of methane, directly entering the sorbent, at a temperature above 850°C, interacts with it according to the reaction (4) - curve 4 in figure 2 a. The interaction is accompanied by the release of H₂, CO₂, H₂O and the binding of residual oxygen while maintaining the residual methane at the outlet of the installation (figure 3).

DTG curves (figure 2 b) show that the reactions with methane occur most intensively (each in its temperature range), then the reduction of zinc oxide with hydrogen, then - reactions with carbon and carbon monoxide, which have approximately the same rates, the target reaction is the least active. The limit of thermal stability of the sorbent in the components of the synthesis gas are shown in Table 1.

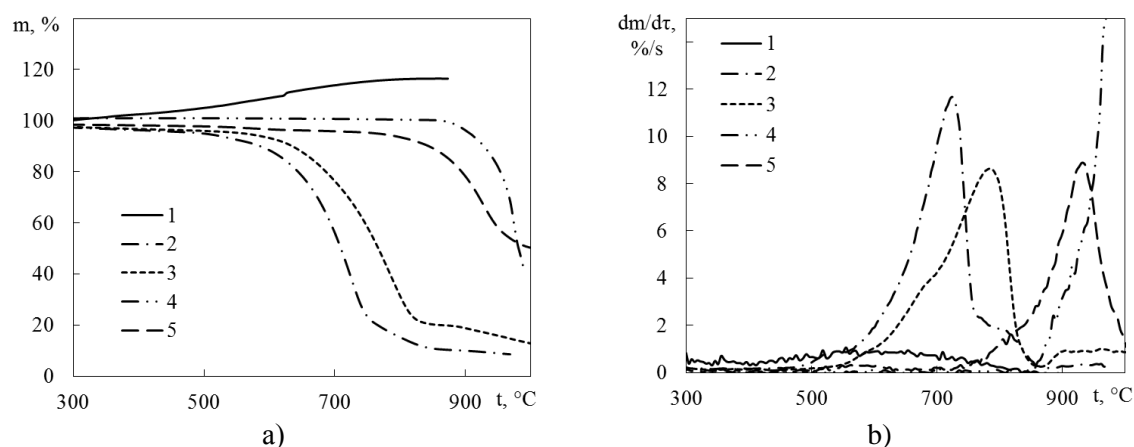


Figure 2. The results of the TGA sorbent based on ZnO in the environments of the components of the synthesis gas: TG-curves (a) and DTG-curves (b). The numbers correspond to the numbers of the reactions.

Table 1. The thermal stability limit of the sorbent based on ZnO.

Reaction number	Reagent, % vol.	The temperature of the onset of significant decomposition of ZnO
2	100% H ₂	509
2	10% H ₂ + 90% Ar	644
3	70% CO + 30% N ₂	561
2	70% H ₂ + 30% Ar	532
4	5% CH ₄ + 95% Ar	853
5	100% C	772

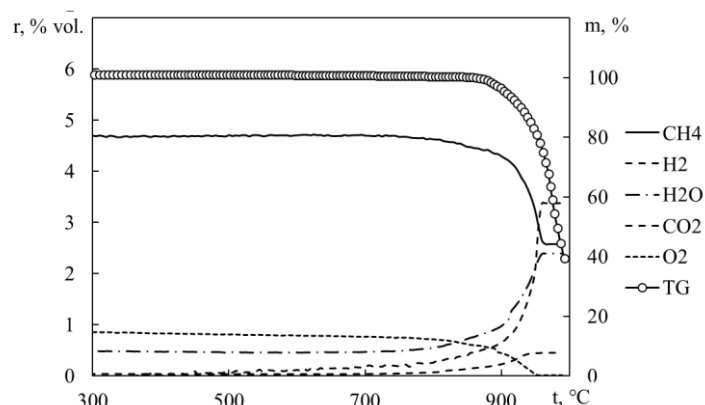


Figure 3. TG curve and gas composition in the interaction of the sorbent with methane.

4. Conclusion

The thermal stability of sorbents based on zinc oxide in a neutral medium was tested in the target temperature range of 400–1000 $^{\circ}\text{C}$. Sorbents showed stability over the entire temperature range. It has been found that at temperatures of 200 and 600 $^{\circ}\text{C}$, non-calcined sorbents emit carbon dioxide. Disposable emissions that do not affect the work of the sorbent.

Analysis of the interaction of zinc oxide with the components of the synthesis gas made it possible to study the intensity of each reaction separately in the target temperature range. At temperatures up to 550 $^{\circ}\text{C}$, the target reaction is basic, and side reactions practically do not develop. When the temperature rises above 550 $^{\circ}\text{C}$, the effect of direct side reactions is observed, leading to the destruction of the sorbent. At 500–550 $^{\circ}\text{C}$ H_2 and CO begin to act, at 750–800 $^{\circ}\text{C}$ - carbon, at 850 $^{\circ}\text{C}$ - methane. The intensity of the reagents action on the degradation of the sorbent is determined by the reactivity of gases to a greater extent than temperature. The most intense destruction produces methane, followed by hydrogen, the least intense destruction occurs as a result of the interaction of the sorbent with carbon monoxide and carbon.

Acknowledgements

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